

Applications of Charge-Step Chronocoulometry

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A preliminary description of the technique of charge-step chronocoulometry has appeared (1). The technique consists of very rapid (0.1 to

(1) F. C. Anson, Anal. Chem., **38**, 1924 (1966).

10 μ seconds) injection of rather large amounts of charge (5-50 μ coulombs/cm²) into an electrode and observing oscilloscopically the resulting open circuit potential-time transient. The potential-time transient are then converted into the corresponding charge-time transient by means of the appropriate charge-potential data so that the time variation of the charge on the electrode is obtained.

If the experiment is performed in the presence of one half of a redox couple, e.g. cadmium ion in a sodium nitrate supporting electrolyte with a mercury electrode, and the charge injected is chosen so that the electrode potential is well out on the diffusion plateau of the corresponding polarogram the rate at which charge is removed from the electrode at open circuit by the resulting faradaic reaction, e.g. $\text{Cd} + 2\text{e}^- = \text{Cd}(\text{Hg})$, will be the diffusion limited rate of transfer of cadmium ion to the electrode surface. Thus the open circuit rate of loss of charge on the electrode will be entirely analogous to the rate of charge accumulation observed in the usual potential-step chronocoulometric experiments (2-5) which are, of course, closed circuit

(2) J. H. Christie, G. Lauer, R. A. Osteryoung and F. C. Anson, Anal. Chem., **36**, 975 (1963).

(3) J. H. Christie, G. Lauer and R. A. Osteryoung, J. Electroanal. Chem., **7**, 60 (1964).

(4) F. C. Anson, Anal. Chem., **36**, 932 (1964).

(5) Ibid, **38**, 54 (1966).

experiments with the electrolysis cell under the control of a potentiostat. Thus, the equation for the charge-time behavior in charge-step chronocoulometry is

$$Q = Q^0 + Q_{\text{inj.}} - 2nFAC\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad (1)$$

where Q^0 is the initial charge on the electrode, $Q_{\text{inj.}}$ is the charge injected, F is the Faraday, n is the number of electrons involved in the electrode reaction, A is the electrode area, C is the bulk concentration of the reactant, D is its diffusion coefficient, and t is the time since charge injection. A plot of $Q - Q^0$ versus the square root of time is linear with an intercept at $t = 0$ corresponding to the injected charge.

The advantages of the open circuit, charge-step method over the closed circuit, potential-step method are these: 1. All problems associated with the resistance in the cell for which the potentiostat is unable to compensate are avoided. In non-aqueous solvents or aqueous solutions having concentrations of supporting electrolyte less than about 0.2 M, where these problems are the most severe, the charge-step method or some other open circuit technique would appear to be the method of choice. 2. Because it is possible to inject charge into an electrode very much faster than its potential can be stepped and held with presently available potentiostats the charge-step method permits experiments to be conducted on much shorter time scales than is true with potential-step techniques so that information about faster electrode processes can be obtained.

Applications of the charge-step technique have been made to the study of reactant adsorption (1, 6) the kinetics of electrode reactions (7), and

(6) F. C. Anson and R. A. Osteryoung, unpublished experiments.

(7) F. C. Anson, unpublished experiments.

the rate of establishment of concentration equilibrium just outside the diffuse double layer when it is abruptly enlarged or diminished (7). In the case of reactant adsorption the equation for the charge time behavior becomes

$$Q - Q^0 = Q_{inj} - 2nFAC \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}} - n\Gamma t \quad (2)$$

where Γ is the amount of adsorbed reactant in moles/cm² and the other symbols are the same as in equation 1. In this case the difference between the intercept of a $Q - Q^0$ versus $t^{\frac{1}{2}}$ and the amount of injected charge, Q_{inj} , gives the amount of reactant adsorbed. An attractive feature of this method is the ability to allow the ionic strength of the solution to become quite low. In a previous study of cadmium adsorption from sodium thiocyanate solutions by potential-step chronocoulometry (8) sodium nitrate was also present "to keep the ionic

(8) F. C. Anson, J. H. Christie, and R. A. Osteryoung, J. Electroanal. Chem., 13, 000 (1967).

strength constant at 1.0", but also because potential-step chronocoulometry may not be safely applied to solutions having ionic strengths below about 0.2. Charge-step chronocoulometry can easily be employed down to ionic strengths of slightly below 0.01 and it would be of considerable interest to compare the values obtained for cadmium adsorption in the presence and absence of nitrate.

When relatively large quantities of charge are injected into an electrode in dilute solutions of electrolytes significant changes in the ionic concentrations just outside the diffuse double layer can occur which alter the resulting potential-time (and charge-time) transients. Due allowance for such perturbations can be made (9) and are essential in applications of charge-

(9) F. C. Anson, experiments to be published.

step chronocoulometry to dilute solutions.